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DVA NOVÉ NÁLEZY GOETHITU Z MELAFYRU V PODKRKONOŠÍ.

TWO NEW FINDS OF GOETHITE IN THE MELAPHYRE OF THE PIEDMONT
REGION OF THE KRKONOŠE.

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Dva nové nálezy goethitu z melafyru v Podkrkonoší.

(S chemickým a polarografickým výzkumem.)

Two New Finds of Goethite in the Melaphyre of the Piedmont Region of the Krkonoše.

(With Chemical and Polarographical Investigation.)

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Obecně rozšířeným nerostem v podkrkonošských melafyrových mandlovcích je jemně paprscitě vláknitý *goethit*, který se zpravidla vyskytuje v malém množství. Je znám téměř ze všech mandlovcovitých facií melafyrových příkrovů. Všude má zřetelně dvojitý výskyt: buď polokulovité až lebníkovité paprscitě vláknité agregáty nebo zcela jemné drobné jehličky, někdy seskupené v chvostky, nepravidelně rozptýlené a uzavřené v krystalech křemene, vyplňujícího částečně nebo úplně dutiny mandlovců.

Goethity z lomu na jz. svahu *Kozákov*, v. od Turnova, i z lomu „Na hrádku“ v Košově, jz. od Lomnice nad Popelkou, mají shodný ráz výskytu a jsou vždycky provázeny krystalovaným *křemenem* a ledvinitým *haematitem*, s nímž je goethit v úzké paragenetické souvislosti.

Agregáty *kozákovského goethitu* jsou tvořeny až 4 cm dlouhými jehlicemi, v jejichž vertikálním pásmu převládá (010) a plochy prismatické ustupují. Jak bylo z nábrusu jasně patrné, přikládají se jehlice k sobě plochami (010). Naproti tomu u *goethitu z Koso*va převládají plochy hranolové nad (010). Terminální plochy nebyly nikde zjištěny. Z *Koso*va jsou známy hojné jehlice uzavřené v krystalech křemene, které jsou buď větší a pak více individualisované, nebo menší a pak seskupeny v jemné chvostky několika jehliček. Vzácně byly zjištěny případy, kdy větší goethitové jehlice vynikají ven z ploch krystalů křemene a jejich vyčnívající části jsou silně hydratisovány.

Svým vznikem náleží *goethit* této paragenese do hydrotermální fáze a vznikl již před krystalisací křemitého gelu v dutinách. Pozdější spontánní krystalisací křemene byly goethitové agregáty uvolněny od podkladu a někdy i úplně roztříštěny.

Chemické prozkoumání vzorků goethitu z Kozákova i z Košova provedl jeden z nás (KOMÁREK) v chemické laboratoři mineralogického oddělení Národního musea v Praze. Bylo zjištěno, že oba analysované vzorky goethitu kromě mechanicky přimíšeného křemene jsou znečištěny jen velice nepatrným množstvím vápníku a hořčíku. Pro zjištění přesného obsahu obou těchto kovů byly vypracovány zcela nové kvantitativní metody, používající ke konečnému stanovení *polarografu*. Principy těchto metod jsou stručně popsány. Vedle dosti podrobného vyličení celého způsobu chemické analýzy jsou připojeny jako doklad i dva polarogramy, ukazující obsah vápníku a hořčíku obou goethitů. Též je přiložen náčrt jednoduchého zařízení, použitého při stanovení hořčíku a nutného pro předběžnou úpravu vzorku před vlastním stanovením polarografickým.

Výsledky provedených analys nelze přesněji srovnávat s rozborů goethitů z druhých nalezišť, neboť analýzy jiných autorů udávají množství vápníku a hořčíku při obsahu skoro vždy jen vyšším než 0,1% CaO resp. MgO. Oba zkoumané vzorky představují velice čistou hmotu goethitovou, provázenou v patrnějším množství jen *kyslíčnickem křemičitým*. Hořčíkem jsou znečištěny poměrně více než vápníkem. Goethit z Košova má obou přímíšenin podstatně méně než goethit z Kozákova.

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The paragenesis of minerals in the melaphyre sheets of the piedmont region of the Krkonoše offers a number of interesting minerals filling fissures and cavities in the amygdaloidal facies of the rock, in which they crystallized from hot minerogenic post-eruptive solutions. A universally distributed mineral, though often occurring only in minute quantities, is the *goethite*, one of the first minerals to crystallize in the form of handsome hemispherical or reniform aggregates composed of fine, slim, radially arranged needles, or it is enclosed in the form of minute tufts or isolated tiny needles in crystals of *quartz*, *smoke-quartz* or *amethyst*. Its occurrence in the *melaphyres* was known already in the second half of last century. The first report of it we find in the mineralogical topography of V. ZEPHAROVICH (21, pp. 257—258), who according to a written communication of M. WEBSKY mentions the find of *goethite* (*pyrrhosiderite*) in the cavities of amygdaloidal *melaphyre* in the old limonite mine at Šono v, east of Broumov, where it occurred in aggregates of the form of kidney ore. The second report on goethite from the *melaphyre* of the piedmont region of the Krkonoše was given by E. BOŘICKÝ (3, p. 69), who described similar, radially columnar aggregates and needles enclosed in *quartz* crystals from Ruprechtice (correctly Roprechtice), NW of Jilemnice. From the younger melaphyre sheets B. KATZER (14, p. 115) mentions goethite needles enclosed in rock crystals from Mt. Levín, N of Nová Paka, and B. BOBKOVÁ (1, p. 15) reports a similar occurrence from the neighbourhood of Žďárek, NW of Hodkovice. From the adjoining part of Silesia finds of goethite in radial aggregates and fine needles in quartz are known from the amygdaloidal melaphyres of the vicinity

of Kladsko and Landshut (today Kamieniógóry). The first report of them was given by A. P. COLEMANN (5, pp. 48—49). — From this it is evident that goethite is distributed through the whole complex of melaphyre eruptives of the Upper Paleozoic. It is however not restricted only to the piedmont region of the Krkonoše, but occurs also elsewhere. This is shown by the records of its occurrence e. g. in the melaphyres of the vicinity of Zwickau in Saxony, whence it was recorded already by A. FRENZEL (7, p. 135) and of Oberkirchen, SSV of Idar in the Rhineland, which is its classical locality, for it was first described more in detail from here by A. BREITHAUP (4, p. 237).

The whole character of the occurrence of *goethite* in *melaphyres* is according to observation made up till now, also of new material, distinctly twofold. There are the above mentioned hemispherical to reniform, radially fibrous aggregates, which are very striking in the fissure fillings of the melaphyre, and also quite fine, minute needles, sometimes grouped in tufts, irregularly scattered and enclosed in quartz crystals. In the amygdaloidal melaphyres of the piedmont region of the Krkonoše goethite occurs in both these forms. K. TUČEK (20, pp. 11—13) mentions briefly some new finds of *goethite*. In addition to them were found abundant tufts of needles enclosed in *quartz* crystals in cavities and fissures of the melaphyre of the area between Rváčov and Morcinov, W and SW of Lomnice nad Popelkou, especially in the wooded slopes S of Morcinov.

Of all the new finds the *goethites* from the *Kozákov* east of Turnov and from *Košov* SW of Lomnice nad Popelkou were chosen for more detailed investigation and chemical and polarographical analyses. Both have the same character of occurrence and are always accompanied by *kidney ore* as well as by crystallized *quartz*. Also in both cases the goethite in the aggregates is bound rather to larger fissures in the rock than to amygdaloidal cavities, and is in close paragenetic connection with the *hematite*. Both are further always surrounded paragenetically by younger crystallized *quartz*, whose crystals are often very imperfectly developed.

Goethite from the Kozákov.

In an old quarry E of Radostný Mlýn, SW of the summit of the *Kozákov*, E of Turnov, the collector J. SOUKUP, of Jičín found in May 1913 one of the most beautiful samples known of *goethite*. It is formed by unusually rich, radially fibrous aggregates of needles up to 4 cm. long, completely overgrown by slightly violet *amethyst* (inv. no. 31.071). These dark brown to blackish brown aggregates have the typical silky, here and there even semimetallic lustre and in thin layers their needles are translucent saturated brown or brownish yellow. The individual, radial aggregates touch along straight limits, distinctly visible and striking to the bare eye. Their contact planes are entirely smooth and of a pitchy lustre. Only in some places can we observe a fine grooving probably caused by a coarser aggregation of flattened needles of goethite. The terminal faces of the needles could not be determined anywhere, already because the aggregates are completely surrounded

and enclosed by quartz. Even a more detailed examination of the ends of the needles in quartz crystals did not yield any positive result. It seems that in the rapid crystallization of the quartz many fine needles projecting from the surface of the aggregate were destroyed.

Already with a small magnification we find that the cross sections of the needles have the usual contour of goethite in the shape of a strongly squeezed hexagon. From this we may conclude that in the vertical zone of the crystals the face (010) and prismatic faces predominate. The crystals of goethite have thus their usual character. The manner of aggregation of the individual needles was studied more in detail in a thin section from an aggregate, strongly etched with hot hydrochloric acid. After etching the crowded cross sections of the needles became at once clearly visible in the shape of strongly squeezed hexagons of an average size of $0,14 \times 0,008$ mm. But the broadest of them measure as much as 0,28 mm. Thus the thickness and width of the needles are accurately determined; compared with their length, 4 cm., their thickness and width are very small. The cross section shows that the aggregation of the goethite needles takes place in one direction, and that the needles lie against each other with the faces (010).

In the thin section the contact of the goethite with the crystallized quartz can be observed in detail. The limit between the two minerals is fairly uneven and both penetrate each other. Tufts of coarse needles penetrate the quartz crystals, and fine-grained quartz penetrates the goethite aggregates in narrow fissures. We might believe that in the aggregate of goethite fine needles and tufts were detached in this process and scattered in the crystallizing quartz. But such a phenomenon was never observed. Against it speak also the relatively small size of the tufts and the fairly clearly visible, independent delimitation of the minute needles which are evidently not merely remains of larger, destroyed crystals. It seems that we have here another form of the goethite, as indicated also by numerous observations of needles and tufts of goethite in the quartz. The goethite aggregates have often fine, long fissures usually running obliquely to the length of the needles and often split along them. These fissures were formed indubitably under the influence of the pressure of the mother rock on the filling of the cavities.

The goethite is completely surrounded by coarsely crystallized, slightly violettish crystals of *quartz* and *amethyst*. Their individual crystals attain a size of up to 2 cm. The amethyst is characterized by the usual cloudy and unequal distribution of the colouring, which is saturated most at the top of the crystal. The goethite aggregate is not completely grown to the wall of the fissure, but is separated from it by a layer, $\frac{1}{2}$ —1 cm. thick, of granular whitish *quartz* and by a layer, 5 mm. thick, of *hematite* firmly attached to the substratum. From this phenomenon, which was observed also in other samples, it is evident that though in the crystallization of the quartz it came partly to the detachment and separation of the goethite aggregate from the substratum, yet the aggregate itself was not more seriously disturbed, just as in other localities.

Goethite from Košov at Lomnice nad Popelkou.

Of entirely the same character as the preceding one is the *goethite* found by J. SOUKUP in the now abandoned quarry "Na hrádku" at Košov, SW of Lomnice nad Popelkou, where its accompaniment by hematite is still more striking, for the two minerals occur here as a rule close beside each other.

The samples from this locality are always flat fissure fillings; their surface is formed by a fine layer of *delessite*. The fillings are again formed predominantly by *quartz* in crystals of up to 1 cm., usually well delimited, in part transparent, sometimes with a brown or violet tinge. In some samples a dihexaedral development could be observed, which is rather frequent in this area of amygdaloidal melaphyres, especially between Morcinov and Rváčov. The zonal edges are almost always blunted by narrow planes of the unit prism.

The *hematite* constantly accompanying the goethite forms aggregates of the form of kidney ore, rarely also stalactitic or reniform aggregates or minute discs enclosed in quartz crystals. It is fine-grained to massive, but here and there it shows fibrosity and in the discs also a spherical arrangement. It has a blackish gray colour, when fresh it has a slightly submetallic lustre. Its discs measure on an average 0,22 mm. and are rarely formed by crowds of minute tabular crystals of the Elba type. Then they form interesting pretty roses. The discs show symptoms of superficial hydration.

The *goethite* occurs here in the two forms mentioned already from the preceding locality. In many samples we see parts of radially fibrous aggregates completely enclosed in granular and crystallized quartz, elsewhere fine tufts and individual needles enclosed in quartz crystals. In general we may say that the occurrence of goethite is here more varied than on the Kozákov. The radial aggregates are formed of individuals 2—3 cm. long and on an average 0,13 mm. broad, of black to blackish brown colour with a semimetallic, when fresh submetallic lustre and with a typical rust yellow streak. In thin fragments they are translucent from yellow to yellowish brown. The surface of the goethite aggregates is rough, the ends of the needles are again partly broken off just as in the goethite from the Kozákov. In the surrounding quartz crystals we see not rarely negative imprints of goethite crystals.

Morphologically the needles of the Košov goethite differ from those of the Kozákov goethite by their cross sections showing a distinct predominance of the prismatic faces above the face (010) in the vertical zone. The needles are in this zone strongly combinationally grooved by the alternation of faces of different prisms, and thus the cross sections of the needles are rounded and have a spindle shape. The face (010) narrows in the direction towards the top of the crystal, which proves its considerable warping. The terminal faces could not be determined, though here and there it was possible to observe indications of imperfect crystal faces, not further determinable in detail, at the ends of the needles. The goethite needles enclosed in quartz crystals are of two types: rather large and isolated or minute, which are as a rule again

grouped into handsome tufts formed by several individuals. The large needles are black with a yellow termination, the minute needles have a yellow to yellowish brown colouring and attain an average size of $0,30 \times 0,02$ mm. Their scattering in the quartz is quite irregular. Rarely also a penetration was observed of the large goethite needles from the quartz crystals outwards. The outward projecting end of such a needle is always strikingly thickened, which is due to its transformation into limonite. This indicates a rapid hydration of the goethite and an increase in circumference of the needle causing the change in its crystal form. Elsewhere a goethite needle in quartz projecting from the crystal was in its whole length closely enveloped by minute lens-shaped crystals of black hematite of entirely the same character as in the discs and roses mentioned above. In this case the goethite is paragenetically an older mineral than is the hematite.

As far as the origin of the goethite in the melaphyres of the piedmont region of the Krkonoše is concerned it is quite incontestable that it belongs to the hydrothermal stage when it crystallized from a relatively cool solution. The tufts of goethite enclosed in quartz crystals are given by O. DOELTER and H. LEITMEIER (6, p. 679) as proof of the direct origin of goethite from a solution, i. e. not by the usual crystallization from colloidal limonite.

The question of the origin of the goethite causes the scientists similar difficulties as its position as a mineral. The decisive role is played here of course by its structure investigated roentgenometrically by J. BÖHM (2); S. GOLDSZTAUB (9) continued BÖHM's investigations and arrived at the conclusion that there exists in nature really only one watery sequi-oxide of iron, which is represented by two crystal-structural modifications: goethite and lepidocrocite. He recommended to designate the goethite by the formula $\text{FeO} \cdot \text{OH}$. On the other hand H. HIMMEL (10) and in accordance with him W. HOPPE (12) recommended the designation $\alpha\text{-FeO} \cdot \text{OH}$ as being more correct. The most recent investigations of goethite and similar minerals by electron microscope were made by R. FRICKE, TH. SCHOON and W. SCHRÖDER (8). But even after these new, very detailed studies uniformity of opinion has not yet been achieved.

From the observations made in a great number of samples of goethite from the two localities mentioned it is evident that the character of the goethite and the form of its occurrence are in both localities roughly the same. Here one can agree with the opinion voiced by J. KAŠPAR (13, pp. 103—104) that the goethite (which he includes together with others under the designation of limonite) as well as the hematite always accompanying it are independent components of the fissure fillings of the melaphyre are were formed already before the crystallization of the silicious gel. He states that the goethite and the hematite are mostly formed quite independently of each other, but that they may also be formed simultaneously. This view is supported also by all observations made in the samples studied. It is also certain that the spontaneous and rapid crystallization of the quartz from the gel caused not only a disturbance of the goethite aggregates but also their detachment from the

substratum and even their scattering into separate fragments as seen in the material from K o š o v (inv. nos. 31.066, 31.067, 31.069, 31.070). It is obvious that in this process also part of the needles were separated and enclosed in the crystallizing quartz. The same applies also to the hematite, whose aggregates are affected in the same way.

As far as the second form of the goethite is concerned, the minute tufts of needles enclosed in the quartz, we have to assume that originally they crystallized independently at the walls of the fissures of the melaphyre and were in the crystallization of the quartz detached from these walls and enclosed in the quartz crystals.

The investigation made up till now of the goethite from the localities in the melaphyres of the piedmont region of the K r k o n o š e entitles us to the opinion that the whole character of the occurrence, the conditions of the origin, and the properties of the goethite are in all these localities very similar.

A chemical analysis of the goethites from the two localities mentioned was made (KOMÁREK) in the chemical laboratory of the Mineralogical Department of the National Museum. Previous to the making of the chemical analysis proper the *density* of the goethites was accurately established. For this purpose samples which did not exteriorly show any admixture of quartz were used in both cases. The density was determined by weighing pieces of about 2 g. in the air and then, after attaching them to a fine wire, in redistilled water. A correction was used also for the volume of the wire immersed with half its length in the water (0,0002 g.).

After accurately determining the weight of the sample immersed in water the piece of mineral examined was in both cases dried roughly by placing it on filter paper and then it was heated in an electric heater for two hours at a temperature of 110° C. Thus the original weight of the sample in the air was accurately achieved again. The whole piece of the sample was then crushed in a steel percussion mortar, first into coarse pieces and then in small quantities into fine fragments. Finally the whole of the sample was pulverized in small quantities in an agate mortar most thoroughly. The very fine, brown powder thus obtained was mixed most perfectly in order to obtain absolute homogeneity of the sample. The pulverization in the agate mortar was carried out most thoroughly, as otherwise the mineral would have resisted for an extremely long time the effect of acids. By grinding the sample to the finest powder much time and acids were saved in the later analysis. At the same time also the danger was lowered, in connection with the use of a lesser quantity of acids, that impurities, if only quite slight ones, would get into the analyzed sample of the minerals, such as may get in a short time into redistilled acids in consequence of their contact with the glass of the bottles in which the acids are kept.

In order to determine the *volatile components* (water) part of the powder of the sample was heated in a porcelain crucible in the electric heater for about 10 hours at 105—110° C. In neither of the two samples of goethite was the slightest loss in weight ascertained. Only then were the samples strongly glowed in the electric oven in bright red glow and

after cooling in the desiccator the loss in weight was determined by weighing, corresponding to the water of the hydrate. As the strongly glowed Fe_2O_3 dissolves in acids only with great difficulty, the glowed residue was not used for any further determination.

It was found by preliminary tests that though the goethite samples had been ground to a very fine powder they resisted very strongly the action of acids. Though it is reported in the literature (6, p. 675), (11) that goethite is dissolved most readily in *nitric acid*, yet both samples resisted very strongly this acid even when it was concentrated and hot. Therefore a process was finally worked out as the most suitable method of analysis in which the very finely ground goethite is heated in a water-bath with concentrated *nitric acid* and *hydrochloric acid* mixed in the volume-ratio of 1:3. The analysis was made in a big quartz crucible covered with a lid concave below so that the drops of acid condensed on it could fall back to the bottom of the crucible. First it was heated only slightly so that both acids could begin to react on each other. Later it was heated more strongly, finally also with the lid removed. The solution formed of ferric salt was carefully poured off into a quartz dish and to the residue of undissolved goethite was added a new dosis of acids, and then we proceeded again as described above.

In the analysis of the goethite acids were used which had been prepared immediately before the analysis by distillation from the purest commercial concentrated acids labelled "pro analysi". In the whole chemical investigation the greatest cleanliness was maintained intentionally and most rigorously, of the reagents used as well as of the receptacles, and great care was also taken in carrying out the analyses as some admixtures (Ca, Mg) had to be accurately determined, and these were present in the samples examined only in quite tiny quantities.

After the complete decomposition of the mineral by acids the content of the quartz dish was evaporated in a water-bath as much as possible, in order to make possible the most complete exclusion of the *silicic acid*. After adding hot water the solution was filtered and divided into two parts. After having been evaporated repeatedly with *hydrochloric acid* the larger part was completely freed from the rest of nitric acid, so that in our further work platinum ware could be used without fear. The smaller part was evaporated repeatedly with concentrated *nitric acid*, and thus completely freed from chlorides, and then used for reactions on *manganese* and *phosphoric acid*. In carrying out the systematic process of the qualitative analysis the usual method was employed. For the reactions on the different elements and components sought as specific reagents as possible were used. In order to economise the material examined only microchemical methods were mostly used, or at least semimicrochemical. Where I worked with glass ware, Jena glass was used.

By *qualitative analysis* it was found that in addition to *water* and *ferric oxide* both goethite samples contain also a certain small quantity of *silicon oxide* and a very small quantity of *calcium* and *magnesium*. With *sulfuretted hydrogen* no precipitate formed in the hydrochloric solution, acidified according to prescription. *Ferric hydro-*

xide precipitated by *ammonium hydroxide* was after dissolving in *hydrochloric acid* in a platinum (not in a porcelain!) dish reprecipitated by an excess of a strong solution of *potassium hydroxide*, and then we heated again to boiling point. But by further working *aluminum* was not found even in traces. The reactions for *phosphoric acid* and *manganese* were also negative. The samples did not contain any carbon dioxide, which would otherwise have indicated an admixture of siderite. Thus the supposition was justified that all iron was present in the analyzed material only as trivalent Fe^{III} and that it would not be necessary to establish separately the share of ferrous oxide, which would have entailed a rather laborious process.

After making the qualitative analysis we proceeded to the *quantitative determination* of the different components. After the complete decomposition of the goethite by acids as described above *silicic acid* was excluded by a double evaporation with hydrochloric acid; by glowing in a platinum crucible it was transferred to silicon dioxide, and its admixture Fe_2O_3 was determined after evaporation with hydrofluoric acid and with a few drops of sulphuric acid. The *iron* was determined gravimetrically in the usual way. The slightly ammoniacal filtrate after the exclusion of iron was evaporated to dryness, and after carefully expelling the ammonium salts it was worked only in the volume of a few cubic centimeters. The *calcium* was precipitated in the usual way as oxalate, the *magnesium* as magnesium ammonium phosphate (after SCHMITZ's method). But with calcium and magnesium such trifling amounts of precipitate were obtained even after working about 1 g. of the sample that by the normal macrochemical manner of analysis it was absolutely impossible to arrive at a certain result. As microbalances were not available in the chemical laboratory of the National Museum and as also the use of BANG's microburet was not satisfactory for such small quantities of substances as it proved not sufficiently accurate, other, highly sensitive methods were tried. Therefore attention was turned to the use of the *polarograph*, though just for the determination of *calcium* and *magnesium* suitable polarographical methods had not yet been elaborated. Thus it was necessary to use for the polarographical determination of calcium as well as of magnesium entirely new working methods, which will be described in detail elsewhere (15), (16), and which were elaborated specifically for the given purpose. In the present article the main principle of the two methods is given only quite briefly, in view of the fact that it will be possible to use them successfully also for the analysis of other minerals for the very accurate determination of trifling amounts of calcium or magnesium.

For the purpose of the quantitative estimation of *calcium* the *calcium oxalate* was precipitated from the solution of a volume of only a few cubic centimeters, separated by means of a centrifuge from the remaining solution which still contained magnesium. The clear, slightly ammoniacal solution with magnesium salt and with the excess of ammonium oxalate was sucked off from the centrifugal cone by a pipette lengthened into a long thin point. The remaining calcium oxalate was

dispersed in about 0,1 ml. of a weak solution of ammonium oxalate and again centrifuged. This was repeated still once more. Then the clear calcium oxalate, which had accumulated in the point of the conical test tube, was dissolved in 50% *nitric acid*; the resulting solution was quantitatively transferred by pipette into a crucible, in which it was then evaporated and the residue glowed. After dissolving the glowed residue in a drop of very diluted *nitric acid* all calcium was excluded by a watery solution of *iodic acid* and an excess of 87% *ethanol*, in the form of iodate. This method will be described in detail in a technical chemical paper (15). After centrifugation and washing of the precipitate with 87% *ethanol* the $\text{Ca}(\text{JO}_3)_2$ thus isolated was dissolved in water, transferred into a 10 ml. graduated flask; 1 ml. m/10 KCl was added as inert electrolyte, and after mixing the neutral solution thus formed was subjected to polarographical electrolysis. The wave height, caused by the reduction of JO'_3 , was compared with the wave height of the solution m/10.000 JO'_3 , which therefore contains in 10 ml. 174 μg JO'_3 . One Ca-atom corresponds here to 2 JO'_3 . The polarographical wave of JO'_3 is six times higher than would correspond to the equivalent amount of the divalent cation (Ca); it is favourably shifted into the region of medium reduction potentials, and it is very well drawn. Thus we achieve not only a great sensitivity but also great accuracy. For preparing m/10.000 JO'_3 a neutral solution of KJO_3 was used to which was added KCl to the same concentration as the one realized in the solutions $\text{Ca}(\text{JO}_3)_2$ tested. To the calculation of the amount of calcium applies that the wave height of the solution m/10.000 JO'_3 (= 174 μg JO'_3 in 10 ml.) corresponds to a concentration of 20 μg of Ca in 10 ml. In excluding the calcium as iodate one has to be careful that oversaturated solutions are not formed (15).

For the quantitative estimation of the *magnesium* the filtrate was after precipitating the calcium oxalate combined with wash liquids, evaporated to dryness, freed by glowing of a great excess of ammonium salts, and after dissolving in a few drops of diluted hydrochloric acid all magnesium was excluded as *magnesium ammonium phosphate* in the usual way (19). After centrifugation the precipitate of magnesium ammonium phosphate was dispersed in 0,1 ml. of distilled water and again centrifuged. This was repeated once more. As a greater quantity of water used for washing would mean a loss of precipitate owing to the perceptible solubility of the precipitate in pure water, the ammonia had to be removed at least from the whole upper and middle parts of the centrifugal cone in another way. Here a simple apparatus described elsewhere in an account of the new methods was used with good results already after the first centrifugation (17). This apparatus was used already when washing the upper and middle parts of the centrifugal cone when isolating $\text{Ca}(\text{JO}_3)_2$ in order to save *ethanol* and to reduce the danger of a loss of precipitate.

The pure precipitate of *magnesium ammonium phosphate* accumulated in the point of the centrifugal test tube was dispersed with a very thin glass rod in 0,1 ml. of water, and then it was neutralized with about m/100 HJO_3 (an accurate concentration is not at all required)

by using a simple capillar pipette with so thin an outflow as to make the solution of *iodic acid* run out from it only when the point is immersed below the level of the liquid. This apparatus, figured in the diagram fig. 1, was recently described separately in the chemical press (18).

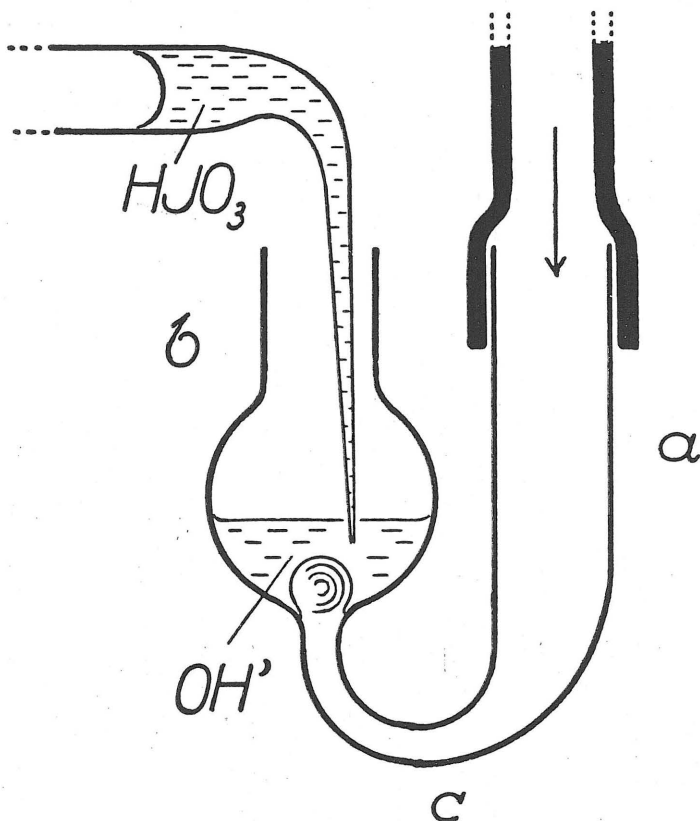
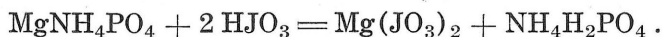


Fig. 1: Arrangement for the neutralization of magnesium ammonium phosphate with a solution of iodic acid by using a pipette with capillary outflow after K. Komárek ($\frac{2}{1}$ scale).

The solution in the course of neutralization is mixed by an air current pressed out by water from a large bottle (wash bottle). As soon as the precipitate begins to disappear, and the solution clears up distinctly, the smallest possible necessary quantity of solution of *methyl orange* is added, and the capillar end of the pipette is immersed in the solution with short intervals until the already slight yellow coloration of the solution turns into a distinctly orange red coloration. Then the solution is transferred quantitatively into a 10 ml. graduated flask, KCl is added, and then one proceeds as with the solution of $\text{Ca}(\text{JO}_3)_2$. The neutralization is expressed by the equation:



From this it follows that one Mg-atom corresponds to two molecules of HJO_3 or to $2\text{JO}'_3$. Therefore here the polarographical wave height obtained is again six times greater than the one corresponding to the reduction of the equivalent amount of divalent cation to metal. The wave height of $m/10.000\text{JO}'_3$ ($= 175\text{ }\mu\text{g JO}'_3$ in 10 ml.) corresponds to a concentration of $12,16\text{ }\mu\text{g Mg}$ in 10 ml. The method is very accurate, and the colour change in the neutral point can be ascertained very sharply, for owing to a fairly strong solution of acid being used it does not come to any more perceptible dilution, in contradistinction to microtitration with very much diluted acids. This new polarographical determination of magnesium was described in detail in a separate chemical article (16).

The following results were obtained by the above investigation and by the polarographical methods mentioned:

	Goethite from the Kozákov: (Invent. no. 31.071)	Goethite from Košov: (Invent. no. 31.063)
Density	4,164	4,215
SiO_2	1,79%	1,22%
Fe_2O_3	87,92%	88,60%
H_2O	10,17%	10,03%
CaO	0,017%	0,004%
MgO	0,057%	0,008%
	99,95	99,86

As illustration of the polarographical investigation are given here two polarograms showing clearly the waves of reduction of JO'_3 , whose

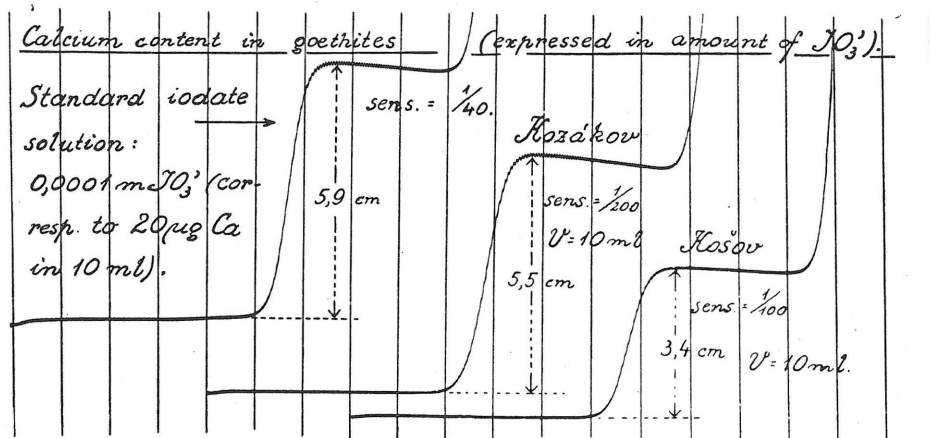


Fig. 2: Calcium content of the goethites expressed in curves of reduction of IO_3' .

height is proportionate to the amount of calcium and magnesium present, in comparison with the standard solution of $m/10.000\text{JO}'_3$ (with a content of KCl) corresponding to a concentration of $20\text{ }\mu\text{g Ca}$ in 10 ml. The solutions investigated were finally diluted to a volume of

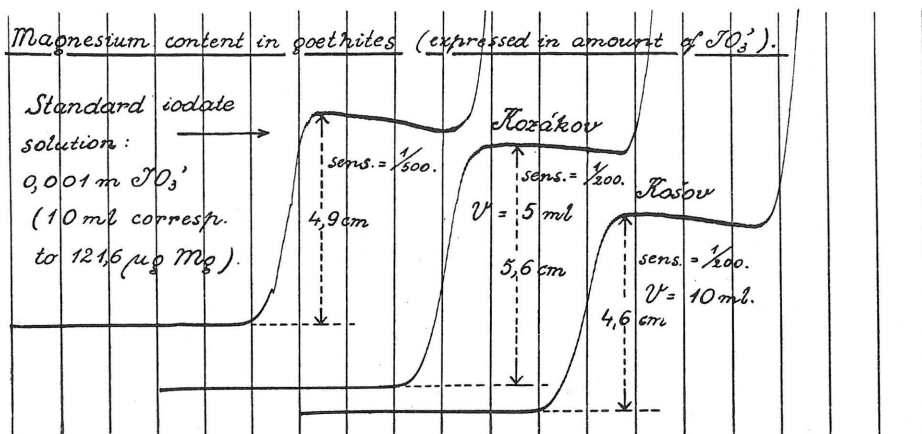


Fig. 3: Magnesium content of the goethites expressed in curves of reduction of IO_3^- .

10 ml or 5 ml (Kozákov — Mg). In the polarographical analysis of the goethite from the Kozákov were used for the determination of the calcium 0,8110 g. of the mineral and for the determination of the magnesium only 0,0811 g. In the analysis of the goethite from Košov were used for the determination of the calcium and magnesium 0,9537 g. of the mineral. The sensitivity of the galvanometer used in the different determinations is given in the polarograms at the corresponding curves. All solutions were alkalinized.

From the results given it can be seen that both samples of goethite represent minerals which in addition to SiO_2 do not contain any other admixtures in more perceptible quantities. The *silicon dioxide* appears to be present in them directly as quartz, disseminated mechanically, even though this admixture is not outwardly visible, so that pieces of the analyzed samples had the appearance of completely pure goethite. As the presence of a perceptible amount of SiO_2 distorts considerably the representation in per cent. of the main components (Fe_2O_3 and H_2O), so that neither their amounts nor even the density of the two samples can be legitimately compared with the ideal values which theoretically apply to entirely pure goethite, the results obtained were recalculated for the two mineral samples without the quartz content. This was done on the supposition that the silicon is not present in the samples investigated as silicate, but only as pure quartz. The admixture of *calcium* and *magnesium* is so trifling that it does not enter here at all into consideration. The amount of quartz present in the two samples was calculated from their contents in silicon dioxide. After making the correction we found for the density of the substance proper of ferric hydroxide in the sample from the Kozákov the value 4,21, for the goethite from Košov 4,27, therefore in both cases lower values than given in the literature for pure goethite (4,28).

	Goethite from the Kozákov:	Goethite from Košov:
Fe ₂ O ₃	89,65%	89,83%
H ₂ O	10,35%	10,17%
	<hr/> 100,00	<hr/> 100,00

Pure goethite corresponding to the formula FeO.OH has the composition:

89,86%	Fe ₂ O ₃
10,14%	H ₂ O
<hr/> 100,00	

(In the encyclopaedia of Doelter-Leitmeier (6, p. 674) is by mistake given the erroneous composition: 89,89% Fe₂O₃ and 11,11% H₂O.)

From this it can be seen that the goethite from the Kozákov contains distinctly more water than the theory demands for pure goethite. The goethite of Košov approaches more closely the ideal composition, and it has also less admixtures. But in both cases we have very pure kinds of goethite, which indubitably were not formed by metamorphism from other kinds of minerals, e. g. from limonite, but were formed directly by crystallization in the cavities of the quartz.

In comparing the analyses of the two goethites here described with the analyses of goethites from other localities the main difficulty is that in the past the authors of analyses hardly ever gave the amount of calcium or magnesium when their oxides were less than 0,1%. Thus f. inst. in Doelter-Leitmeier's encyclopedia (l. c.) only two out of fifty-five analyses indicate an amount of CaO of less than 0,1%, and the amount of MgO is given only in one analysis (analyzed by E. Posnjak and H. E. Merwin). Generally the two elements are not even listed in the tables of the analyses. This can be accounted for by the lack of suitable quantitative methods for the estimation of small amounts of calcium or magnesium. In the international mineralogical literature of the last twenty years no more detailed analyses of goethites are unfortunately given, so that a comparison of results is not possible; such comparisons would be desirable especially in cases of goethites from melaphyres or similar localities.

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The Plate: Radially fibrous aggregates of goethite from the Kozákov east of Turnov. (Collection of the Mineralogical Department of the National Museum, Prague, inv. no. 31.071. Enlarged by one third. Phot. Dr. A. Pilát.)

Detail of the same specimen. (2 × nat. size. Phot. Dr. A. Pilát.)

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